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***trans*-4,4a,6,7,8,8a-Hexahydro-8a-methyl-naphtho[2,3-*b*]furan-5,9(5*H*,9*H*)-dione**

JAYANTA KUMAR RAY AND GANDHI KUMAR KAR

Department of Chemistry, Indian Institute of Technology, Kharagpur 721 302, India

GUR DAYAL NIGAM

Department of Physics and Meteorology, Indian Institute of Technology, Kharagpur 721 302, India

KANDASAMY SIVAKUMAR† AND HOONG-KUN FUN*

X-ray Crystallography Laboratory, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia

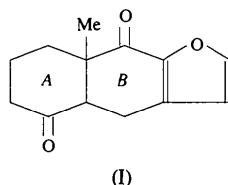
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Abstract

The structure determination of the title compound, C₁₃H₁₄O₃, reveals its *trans* nature. One six-membered ring adopts a chair conformation and the other adopts an intermediate conformation between half-chair and sofa. The crystal structure is stabilized by C—H···O hydrogen bonds.

Comment

Linearly fused tricyclic furan derivatives are found in many sesquiterpenes isolated from marine sponges and are potentially bioactive (Fraga, 1990; Honan, 1985; Jacobi, Craig, Walker, Arriek & Fechette, 1984). We have developed a unique method of mixed-acid catalysed cyclization of furocarboxylic acid derivatives to obtain the tricyclic furodiketones (Ray, Kar, Sami & Chakraborty, 1994). We are interested in the stereochemistry of *A/B* ring junction in order to determine whether the compound is a *cis* or *trans* isomer. Since our NMR study of the title tricyclic furodiketone, (I), in solution did not result in a confirmed stereochemical assignment, we have carried out the X-ray structure analysis and present our results here.



An ORTEPII (Johnson, 1976) diagram of the molecule with the numbering scheme is shown in Fig. 1. The molecule is the *trans* isomer; the C13—C5—C12—H12 torsion angle is 179 (1)°. The five-membered ring is planar whereas one of the two six-membered rings, *A* (C1—C5, C12), has a chair conformation and the other ring, *B* (C5—C7, C10—C12), has an intermediate conformation between half-chair and sofa, with more tendency towards half-chair; the asymmetry parameters are $\Delta C_2(C5—C12) = 0.0474(6)$ and $\Delta C_5(C7) = 0.0788(7)$ (Nardelli, 1983a).

The C—C single-bond distances in this structure have different magnitudes; the two shortest values are 1.441 (2) for C6—C7 and 1.492 (2) Å for C10—C11. The very short C6—C7 bond length shows the presence of conjugation between the five-membered ring and the keto group (O2). The two carbonyl O atoms have different C=O distances, C1=O1 1.209 (2) and C6=O2 1.219 (2) Å. While O1 is not involved in any short contacts, O2 is involved in intermolecular C—H···O hydrogen bonds with C2, C8 and C9 of different molecules surrounding it. The longer C6=O2 distance and the C—H···O hydrogen bonds may result from the conjugation present in that part of the structure.

The molecules are stacked as planar layers parallel to (302) planes in the crystal lattice. In each plane, the molecules are linked by C8—H8···O2 and C9—H9···O2 contacts, whereas the C2—H2B···O2 hydro-

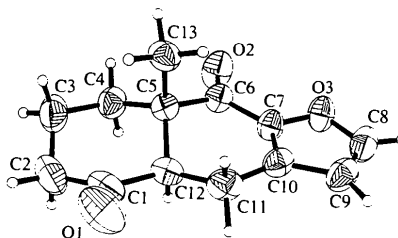


Fig. 1. Structure of the title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme.

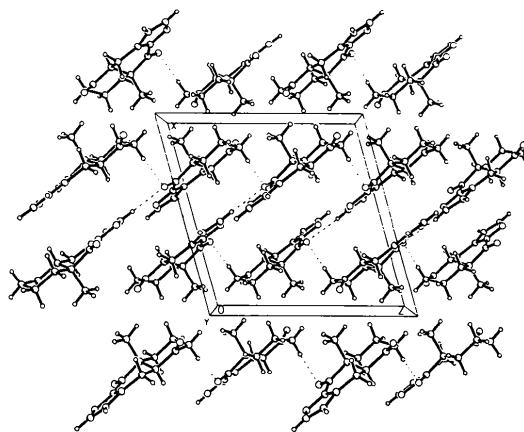


Fig. 2. Packing of the molecules viewed down the *b* axis. The C—H···O hydrogen bonds are shown by dashed lines.

† On leave from: Department of Physics, Anna University, Madras 600 025, India.

gen bond cross-connects the parallel planes. The details are: C2—H2B 0.98 (2), C2···O2ⁱ 3.452 (3), H2B···O2ⁱ 2.55 (2) Å and C2—H2B···O2ⁱ 152 (2)^o; C8—H8 0.94 (2), C8···O2ⁱⁱ 3.347 (2), H8···O2ⁱⁱ 2.47 (2) Å and C8—H8···O2ⁱⁱ 155 (2)^o; C9—H9 0.94 (2), C9···O2ⁱⁱⁱ 3.392 (2), H9···O2ⁱⁱⁱ 2.50 (2) Å and C9—H9···O2 158 (2)^o [symmetry codes: (i) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$; (iii) $x, y - 1, z$]. From the above details, it can be observed that contacts C8···O2 and C9···O2 are stronger than C2···O2, since they arise from a π -conjugated portion of the molecule.

Experimental

Single crystals were obtained by slow evaporation from benzene–petroleum ether (60–80°) mixture.

Crystal data

C₁₃H₁₄O₃
M_r = 218.24
 Monoclinic
*P*2₁/*c*
a = 12.119 (1) Å
b = 7.821 (1) Å
c = 12.107 (1) Å
 β = 105.73 (1)^o
V = 1104.6 (2) Å³
Z = 4
D_x = 1.312 Mg m⁻³

Mo K α radiation
 λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 8–25°
 μ = 0.093 mm⁻¹
T = 293 (2) K
 Thin plate
 0.64 × 0.60 × 0.20 mm
 Colourless

Data collection

Siemens P4 diffractometer
 $\theta/2\theta$ scans
 Absorption correction: none
 3245 measured reflections
 2497 independent reflections
 1743 observed reflections
 $|I| > 2\sigma(I)$
R_{int} = 0.0175

θ_{\max} = 27.50°
 $h = -15 \rightarrow 15$
 $k = -10 \rightarrow 1$
 $l = -1 \rightarrow 15$
 3 standard reflections monitored every 100 reflections
 intensity decay: < 4%

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)] = 0.0424$
 $wR(F^2) = 0.1209$
S = 0.999
 2497 reflections
 201 parameters
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0740P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.163 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.203 \text{ e } \text{Å}^{-3}$
 Extinction correction: none
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
O1	0.11814 (12)	-0.2186 (2)	0.16226 (11)	0.0896 (5)
O2	0.35712 (10)	0.18023 (13)	0.56778 (10)	0.0670 (3)
O3	0.44895 (8)	-0.14016 (13)	0.65720 (8)	0.0553 (3)

C1	0.16947 (13)	-0.0920 (2)	0.20510 (12)	0.0596 (4)
C2	0.1521 (2)	0.0791 (3)	0.14662 (15)	0.0733 (5)
C3	0.1345 (2)	0.2226 (3)	0.22558 (15)	0.0675 (5)
C4	0.22519 (14)	0.2187 (2)	0.33985 (14)	0.0537 (4)
C5	0.23169 (10)	0.0456 (2)	0.40047 (10)	0.0397 (3)
C6	0.32781 (11)	0.0495 (2)	0.51289 (11)	0.0435 (3)
C7	0.37472 (10)	-0.1166 (2)	0.55010 (12)	0.0445 (3)
C8	0.46818 (13)	-0.3125 (2)	0.6655 (2)	0.0587 (4)
C9	0.41069 (13)	-0.3939 (2)	0.5706 (2)	0.0565 (4)
C10	0.34912 (11)	-0.2669 (2)	0.49389 (12)	0.0455 (3)
C11	0.27058 (15)	-0.2757 (2)	0.37551 (14)	0.0549 (4)
C12	0.25731 (11)	-0.0978 (2)	0.32150 (11)	0.0455 (3)
C13	0.12011 (11)	0.0092 (2)	0.43367 (13)	0.0501 (3)

Table 2. Selected geometric parameters (Å, °)

O1—C1	1.209 (2)	C5—C6	1.533 (2)
O2—C6	1.2185 (15)	C5—C13	1.538 (2)
O3—C8	1.367 (2)	C5—C12	1.558 (2)
O3—C7	1.375 (2)	C6—C7	1.441 (2)
C1—C2	1.502 (3)	C7—C10	1.352 (2)
C1—C12	1.519 (2)	C8—C9	1.333 (2)
C2—C3	1.526 (3)	C9—C10	1.425 (2)
C3—C4	1.516 (2)	C10—C11	1.492 (2)
C4—C5	1.532 (2)	C11—C12	1.527 (2)
C8—O3—C7	104.86 (12)	O2—C6—C5	122.69 (11)
O1—C1—C2	122.52 (15)	C7—C6—C5	113.57 (10)
O1—C1—C12	121.5 (2)	C10—C7—O3	111.12 (11)
C2—C1—C12	115.92 (13)	C10—C7—C6	127.57 (12)
C1—C2—C3	112.68 (14)	O3—C7—C6	121.15 (11)
C4—C3—C2	111.55 (14)	C9—C8—O3	111.60 (14)
C3—C4—C5	112.67 (13)	C8—C9—C10	106.77 (14)
C4—C5—C6	109.60 (10)	C7—C10—C9	105.63 (13)
C4—C5—C13	110.73 (12)	C7—C10—C11	121.54 (12)
C6—C5—C13	106.38 (10)	C9—C10—C11	132.82 (13)
C4—C5—C12	109.57 (11)	C10—C11—C12	109.60 (11)
C6—C5—C12	109.23 (10)	C1—C12—C11	112.97 (12)
C13—C5—C12	111.28 (11)	C1—C12—C5	109.98 (11)
O2—C6—C7	123.65 (12)	C11—C12—C5	114.08 (11)
C1—C2—C3—C4	48.9 (2)	C5—C6—C7—C10	5.0 (2)
C2—C3—C4—C5	-55.2 (2)	C6—C7—C10—C11	4.9 (2)
C3—C4—C5—C12	58.1 (2)	C7—C10—C11—C12	16.7 (2)
C4—C5—C12—C1	-54.26 (14)	C10—C11—C12—C5	-47.8 (2)
C5—C12—C1—C2	51.4 (2)	C11—C12—C5—C6	57.54 (15)
C12—C1—C2—C3	-48.8 (2)	C12—C5—C6—C7	-34.17 (14)

All the H atoms were located from a difference Fourier map and refined isotropically.

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1985). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: ORTEPII (Johnson, 1976); SHELXTL/PC (Sheldrick, 1990). Software used to prepare material for publication: SHELXL93. Geometric calculations: PARST (Nardelli, 1983b).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1184). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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4-Phenyl-6,7,8,9-tetrahydro-[1]benzothieno-[3,2-*e*][1,2,4]triazolo[4,3-*a*]pyrimidin-5(4*H*)-one

RAMASAMY VELAVAN AND KANDASAMY SIVAKUMAR†

*Department of Physics, Anna University,
Madras 600 025, India*

URVISH S. PATHAK, KISHOR S. JAIN AND SANJAY SINGH

*Department of Pharmaceutical Chemistry,
L. M. College of Pharmacy, Ahmadabad 380 009,
India*

HOONG-KUN FUN

*X-ray Crystallography Laboratory, School of Physics,
Universiti Sains Malaysia, 11800 USM, Penang,
Malaysia*

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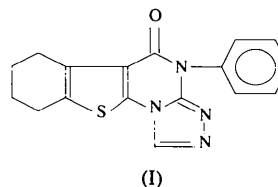
Abstract

The cyclohexane ring of the title compound, C₁₇H₁₄N₄O₃, shows disorder with an 85% major conformer and a 15% minor conformer. Both adopt half-chair conformations. The phenyl ring is tilted by 80.79 (4)° to the plane formed by the rest of the atoms of the mol-

ecule. Molecules of the same orientation are linked by C—H···O hydrogen bonds and short S···O contacts, forming chains along the *b* axis.

Comment

Condensed [1,2,4]triazoles are biologically important compounds (Kottke, Kuesmstedt, Hagen, Renner & Schnitzler, 1983; Francis & Gelotte, 1988; Francis *et al.*, 1988). Since our interest is in the synthesis and characterization of biologically active heterocyclic compounds, especially thienopyrimidines, we have prepared a series of [4,3-*a*]thieno[1,2,4]triazolo[3,2-*e*]pyrimidin-5(4*H*)-one derivatives and studied both their depressant effect on the central nervous system and their analgesic activities (Pathak, Gandhi, Singh, Warde & Jain, 1992). The structure of the title compound, (I), one of these derivatives, has been determined in order to elucidate the conformational features of the molecule. To our knowledge, this is the first crystal structure report of a [1,2,4]triazolo- or thienopyrimidine derivative.



The bond lengths and angles in the title compound have normal values. The part of the molecule comprising the thiene, pyrimidine and triazo rings is planar, with a maximum deviation of 0.050 (2) Å for atom C15. Atoms C2 and C5 also lie close to this plane and the phenyl ring is almost perpendicular to it [dihedral angle

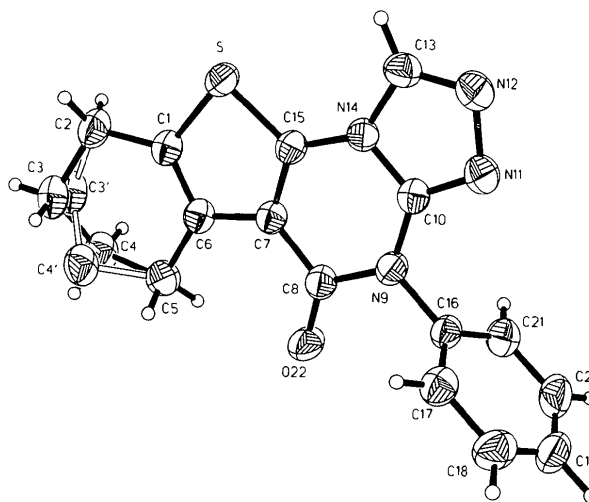


Fig. 1. The structure of the title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme. The minor conformer positions are linked by open bonds.

† Visiting Post Doctoral Research Fellow at the X-ray Crystallography Laboratory, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia.